

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号  
特開2000-228222  
(P2000-228222A)

(43) 公開日 平成12年8月15日 (2000.8.15)

(51) Int.Cl. <sup>7</sup>	識別記号	F I	テーマコード* (参考)
H 0 1 M 10/40		H 0 1 M 10/40	Z 5 H 0 0 3
			A 5 H 0 1 4
H 0 1 G 9/038		4/02	C 5 H 0 2 9
9/058			D
H 0 1 M 4/02		4/58	
審査請求 未請求 請求項の数 6 O L (全 5 頁) 最終頁に続く			

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(54) 【発明の名称】 二次電源

(57) 【要約】

【課題】高耐電圧、高容量、かつ急速充放電特性に優れた二次電源の提供。

【解決手段】活性炭を含む正極と、活性炭とリチウムイオンを吸蔵、脱離しうる炭素材料を含む負極と、第4級オニウム塩とリチウム塩とを含む有機電解液と、を有する二次電源。

## 【特許請求の範囲】

【請求項1】活性炭を含む正極と、活性炭とリチウムイオンを吸蔵、脱離しうる炭素材料とを含む負極と、第4級オニウム塩とリチウム塩とを含む有機電解液と、を有することを特徴とする二次電源。

【請求項2】負極中に活性炭は、活性炭と前記炭素材料との含量中に10～80重量%含まれる請求項1に記載の二次電源。

【請求項3】有機電解液には、第4級オニウム塩が0.5～2.5mol/L、リチウム塩が0.5～2.0mol/L含まれる請求項1又は2に記載の二次電源。

【請求項4】正極には、V、Fe、Co、Mn、Ni、W及びZnからなる群から選ばれる1種以上とリチウムとを含むリチウム含有遷移金属酸化物が含まれる請求項1、2又は3に記載の二次電源。

【請求項5】リチウム含有遷移金属酸化物が、 $\text{Li}_x\text{Co}_y\text{Ni}_{1-y}\text{O}_2$ 又は $\text{Li}_z\text{Mn}_2\text{O}_4$ （ただし、 $0 < x < 2$ 、 $0 \leq y \leq 1$ 、 $0 < z < 2$ 。）である請求項4に記載の二次電源。

【請求項6】リチウム含有遷移金属酸化物は、正極中に5～80重量%含まれる請求項4又は5に記載の二次電源。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、耐電圧が高く、容量が大きく、急速充放電サイクル信頼性の高い二次電源に関する。

## 【0002】

【従来の技術】従来の電気二重層キャパシタの電極には、正極、負極ともに活性炭を主体とする分極性電極が使用されている。電気二重層キャパシタの耐電圧は、水系電解液を使用すると1.2V、有機系電解液を使用すると2.5～3.3Vである。電気二重層キャパシタのエネルギーは耐電圧の2乗に比例するので、耐電圧の高い有機電解液の方が水系電解液より高エネルギーである。

【0003】しかし、有機電解液を使用した電気二重層キャパシタでもそのエネルギー密度は鉛蓄電池等の二次電池の1/10以下であり、さらなるエネルギー密度の向上が必要とされている。電気二重層キャパシタのエネルギー密度向上には電圧を高くすることが最も効果的であるが、電圧を高くすると電解液の分解が起こり寿命に大きく影響を及ぼす。

## 【0004】

【発明が解決しようとする課題】そこで本発明は、高耐電圧かつ高容量でエネルギー密度が高く、充放電サイクル信頼性の高い二次電源を提供することを目的とする。

## 【0005】

【課題を解決するための手段】本発明は、活性炭を含む正極と、活性炭とリチウムイオンを吸蔵、脱離しうる炭素材料とを含む負極と、第4級オニウム塩とリチウム塩

とを含む有機電解液と、を有することを特徴とする二次電源を提供する。

【0006】本明細書において、活性炭又は活性炭とリチウム含有遷移金属酸化物を含む正極と集電体とを接合して一体化させたものを正極体という。負極体についても同様の定義とする。また、二次電池も電気二重層キャパシタも二次電源の1種であるが、本明細書では、正極に活性炭を含み、負極に活性炭とリチウムイオンを吸蔵、脱離しうる炭素材料を含む特定の構成の二次電源を単に二次電源という。

【0007】本発明の二次電源では、充電時には、正極では電解液中のアニオンが活性炭に吸着し、負極では活性炭にリチウムイオンと第4級オニウムイオンが吸着し、リチウムイオンを吸蔵、脱離しうる炭素材料にリチウムイオンが吸蔵される。なお、本明細書では、吸着とは充電時に電気二重層形成によるイオンの活性炭への吸着をいい、イオンが電極に取り込まれると同時に電荷移動を伴う反応を吸蔵という。また、放電時に活性炭からイオンが離れることを脱着といい、イオンが離れると同時に電荷移動を伴うものを脱離という。

【0008】この二次電源の放電時には、正極では活性炭に吸着しているアニオンの脱着が起こり、負極では活性炭に吸着しているリチウムイオンと第4級オニウムイオンの脱着が起こる。第4級オニウムイオンは活性炭から脱着しやすいが、リチウムイオンは全ては脱着せずに、活性炭に一部残存する。そのため、放電終了時の負極の電位は、初めの充電前の負極の自然電位より単になる。

【0009】その後、再び充電すると、上記活性炭には活性炭本来の自然電位より単な電位から第4級オニウムイオンの吸着が起こる。すなわち、自然電位より単な電位で負極の充電ができるので、二次電源の耐電圧を高められる。

【0010】リチウムイオンを吸蔵、脱離しうる炭素材料は、一般に負極活物質として使用すると、リチウムイオンが炭素材料へ吸蔵及び脱離する電気化学反応により大容量が得られるが、大電流で放電すると容量低下が著しい。ところが、本発明における負極のリチウムイオンを吸蔵、脱離しうる炭素材料は、比較的小電流による充電時及び放電時はそれぞれリチウムイオンを吸蔵及び脱離するが、大電流による充放電の場合はほとんど反応しない。本発明の二次電源では、大電流による充放電の場合は、活性炭に対するイオンの吸脱着の物理反応が起こる。物理反応の場合、容量は小さいが大電流充放電を繰り返しても容量低下が少ない。

【0011】すなわち、本発明では、高容量のリチウムイオンを吸蔵、脱離しうる炭素材料と、低容量ではあるが大電流充放電に対し容量低下が少ない活性炭との混合物を負極に使用することにより、高容量でありかつ大電流放電による容量低下が少ない負極となりうる。

【0012】負極に含まれる活性炭の量は、活性炭とリチウムイオンを吸蔵、脱離しうる炭素材料との含量中に10～80重量％が好ましい。10重量％未満では、大電流放電による二次電源の容量の低下が著しい。80重量％超では、負極自体の容量が小さくなり、二次電源の容量を大きくできない。活性炭の量は、特に30～70重量％が好ましい。

【0013】本発明では、有機電解液中にはカチオンとして第4級オニウムイオンとリチウムイオンが含まれる。第4級オニウムイオンとしては、第4級アンモニウムイオン又は第4級ホスホニウムイオンが好ましく、特に $(C_2H_5)_4P^+$ イオン、 $(C_2H_5)_4N^+$ イオン、 $(C_2H_5)_3(CH_3)N^+$ イオン等が好ましい。

【0014】また、第4級オニウム塩及びリチウム塩のアニオンであって有機電解液中に含まれるアニオンは、 $PF_6^-$ 、 $BF_4^-$ 、 $ClO_4^-$ 、 $N(CF_3SO_2)_2^-$ 、 $CF_3SO_3^-$ 、 $C(SO_2CF_3)_3^-$ 、 $AsF_6^-$ 及び $SbF_6^-$ からなる群から選ばれる1種類以上が好ましく、特に $BF_4^-$ が好ましい。なお、第4級オニウム塩のアニオンとリチウム塩のアニオンは同じでも異なってもよい。

【0015】有機電解液に含まれる第4級オニウム塩及びリチウム塩の濃度は、第4級オニウム塩が0.5～2.5mol/L、リチウム塩が0.5～2.0mol/Lであることが好ましく、特にリチウム塩が0.8～1.5mol/L、リチウム塩が0.8～1.5mol/Lであることが好ましい。

【0016】有機電解液の溶媒は、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネート、ジメチルカーボネート、エチルメチルカーボネート、ジエチルカーボネート、スルホラン及びジメトキシエタンからなる群から選ばれる1種以上が好ましい。

【0017】正極及び負極に含まれる活性炭は同じでも異なってもよいが、いずれも比表面積が300～3000 $m^2/g$ であることが好ましい。活性炭の原料、賦活条件は特に限定されず、例えば原料としてはやしがら、フェノール樹脂、石油コークス等が挙げられ、賦活方法としては水蒸気賦活法、熔融アルカリ賦活法等が挙げられる。

【0018】本発明の二次電源の容量を高めるには、正極にリチウム含有遷移金属酸化物が含まれることが好ましい。V、Fe、Co、Mn、Ni、W及びZnからなる群から選ばれる1種以上とリチウムとのリチウム含有遷移金属酸化物が好ましく、特に $Li_xCo_yNi_{1-y}O_2$ 又は $Li_zMn_2O_4$ （ただし、 $0 < x < 2$ 、 $0 \leq y \leq 1$ 、 $0 < z < 2$ 。）が好ましい。リチウム含有遷移金属酸化物が含まれることにより正極の容量が高まり、それに合わせて負極のリチウムイオンを吸蔵、脱離しうる炭素材料の量を増大させると、二次電源はより高容量にできる。

【0019】正極中のリチウム含有遷移金属酸化物の量

は、活性炭とリチウム含有遷移金属酸化物の含量の5～80重量％が好ましい。5重量％未満であると、リチウム含有遷移金属酸化物が正極に含まれる効果が小さく、二次電源の電圧を高められない。80重量％を超えると、相対的に正極中の活性炭の量が少なくなるため、充放電サイクルにおける容量減少が著しくなる。より好ましくは10～60重量％である。

【0020】また、正極の抵抗を低くするために、正極中に導電材として導電性のカーボンブラック又は黒鉛が含まれることが好ましい。このとき、導電材は正極中に0.1～20重量％含まれることが好ましい。

【0021】本発明において負極に含まれるリチウムイオンを吸蔵脱離しうる炭素材料は、X線回折測定による【002】面の面間隔が0.335～0.410nmであることが好ましい。面間隔が0.410nm超の炭素材料は充放電サイクルにおいて劣化しやすい。具体的には石油コークス、メソフェーズピッチ系炭素材料又は気相成長炭素繊維を800～3000℃で熱処理した材料、天然黒鉛、人造黒鉛、難黒鉛性炭素材料等が挙げられる。

【0022】正極体の作製方法としては、例えば活性炭粉末と導電材としてのカーボンブラックとバインダとしてのポリテトラフルオロエチレンとの混合物を混練した後、シート状に成形して正極とし、この正極を集電体に導電性接着剤を用いて固定する方法がある。また、バインダとしてポリフッ化ビニリデン、ポリアミドイミド、ポリイミド等を溶解したワニスに、活性炭粉末とカーボンブラックを分散させ、これをドクターブレード法等によって集電体上に塗工し、乾燥して得てもよい。正極にリチウム含有遷移金属酸化物が含まれる場合は、上記の活性炭粉末のかわりに活性炭粉末とリチウム含有遷移金属酸化物粉末との混合物を用いて同様に作製できる。

【0023】正極に含まれるバインダの量は、正極体の強度と容量等の特性とのバランスから1～20重量％であることが好ましい。また、負極体も正極体と同様にして作製することが好ましく、負極体に含まれるバインダの量も1～20重量％が好ましい。

【0024】

【実施例】次に、実施例（例1～4）及び比較例（例5）により本発明をさらに具体的に説明するが、本発明はこれらにより限定されない。なお、例1～5におけるセルの作製及び測定はすべて露点が-60℃以下のアルゴングローブボックス中で行った。

【0025】【例1】フェノール樹脂を原料として水蒸気賦活法によって得られた比表面積2000 $m^2/g$ の活性炭を80重量％、導電性カーボンブラックを10重量％、及びバインダとしてポリテトラフルオロエチレンを10重量％からなる混合物をエタノールを加えて混練し、圧延した後、200℃で2時間真空乾燥して厚さ150 $\mu m$ の電極シートを得た。このシートをポリアミド

イミドをバインダとする導電性接着剤を用いてアルミニウム箔に接合し、減圧下で300℃で2時間熱処理し、正極体とした。なお、電極面積は24cm<sup>2</sup>とした。

【0026】正極体に使用した活性炭を70重量%、石油コークスを熱処理することによって得られる【002】面の面間隔が0.344nmでありリチウムイオンを吸蔵、脱離しうる炭素材料を10重量%、カーボンブラックを10重量%、及びバインダとしてポリテトラフルオロエチレンを10重量%からなる混合物をエタノールを加えて混練し、正極と同様の方法で厚さ150μmの電極シートを作製した。このシートを正極同様、ポリアミドイミドをバインダとする導電性接着剤を用いて銅箔に接合し、減圧下で300℃で2時間熱処理し、負極体とした。なお、電極面積は24cm<sup>2</sup>とした。

【0027】上記正極体と上記負極体とを、ポリプロピレン製不織布セパレータを介して対向させ挟持して素子を作製した。プロピレンカーボネートに1mol/Lの(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>(CH<sub>3</sub>)NBF<sub>4</sub>と1mol/LのLiBF<sub>4</sub>を溶解した溶液を電解液とし、該電解液に前記素子を十分に含浸させ、初めに3.2Vで24時間充電し、その後1Vまで放電した。次に3.2Vから1Vまでの範囲で初期容量を測定した。その後、充放電電流240mAで、3.2Vから1Vまでの範囲で充放電サイクル試験を行い、2000サイクル後の容量を測定し、容量変化率を算出した。結果を表1に示す。

【0028】【例2】負極の電極シートの混合比を、活性炭を40重量%、リチウムイオンを吸蔵、脱離しうる炭素材料を40重量%、カーボンブラックを10重量%、及びバインダとしてポリテトラフルオロエチレンを10重量%に変更した以外は例1と同様にして負極体を得た。この負極体を用いた以外は例1と同様にして素子を作製し、例1と同様に電解液を含浸させた。この素子を用いて例1と同様に評価した。結果を表1に示す。

【0029】【例3】活性炭を80重量%、導電性カーボンブラックを10重量%及びポリテトラフルオロエチレンを10重量%の混合物のかわりに、活性炭を60重量%、LiCoO<sub>2</sub>を20重量%、導電性カーボンブラ

ックを10重量%及びポリテトラフルオロエチレンを10重量%の混合物を使用した以外は例1と同様にして正極体を得た。

【0030】上記正極体を用いた以外は例1と同様にして素子を作製し、例1と同様に評価した。結果を表1に示す。

【0031】【例4】LiCoO<sub>2</sub>のかわりにLiCo<sub>0.2</sub>Ni<sub>0.8</sub>O<sub>2</sub>を用いた以外は例3と同様にして正極体を得た。この正極体を用いた以外は例1と同様にして素子を作製し、例1と同様に評価した。結果を表1に示す。

【0032】【例5】正極体にも負極体にも例1で得られた正極体を用いた以外は例1と同様にして素子を作製し、例1と同様にして容量を測定し、例1と同様に評価した。結果を表1に示す。

【0033】

【表1】

	初期容量 (mAh)	容量変化率 (%)
例1	4.83	-8.6
例2	6.32	-9.8
例3	11.7	-9.9
例4	12.6	-10.2
例5	3.64	-54.7

【0034】

【発明の効果】本発明の二次電源は、負極において、比較的大きな電流での充放電では第4級オニウムイオンが吸着、脱着し、比較的小きな電流での充放電ではリチウムイオンを吸蔵、脱離しうる炭素材料にリチウムイオンが吸蔵、脱離する。そのため、大きな電流での充放電によるリチウムイオンを吸蔵、脱離しうる炭素材料の劣化が少なく、急速充放電特性に優れている。

【0035】また、負極に含まれる活性炭の電位は自然電位より卑になっているので、本発明の二次電源は耐電圧が高い。さらに、負極にリチウムイオンを吸蔵、脱離しうる炭素材料が含まれているため、高容量である。

フロントページの続き

(51)Int. Cl.<sup>7</sup>

H01M 4/02  
4/58

識別記号

FI

H01G 9/00

ターコード(参考)

301D

301A

Fターム(参考) 5H003 AA01 AA02 AA04 AA10 BB01  
BB05 BD00 BD04 BD06  
5H014 AA02 EE08 EE10 HH00 HH01  
HH08  
5H029 AJ02 AJ03 AJ05 AJ12 AK03  
AL06 AM03 AM04 AM07 DJ09  
HJ10

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 CLAIMS
 

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[Claim(s)]

[Claim 1] The secondary power supply characterized by having the organic electrolytic solution containing the positive electrode containing activated carbon, activated carbon and the negative electrode which contains occlusion and the carbon material from which it may be desorbed for a lithium ion, and the 4th class onium salt and lithium salt.

[Claim 2] It is the secondary power supply according to claim 1 by which activated carbon is contained ten to 80% of the weight in the total amount of activated carbon and the aforementioned carbon material in a negative electrode.

[Claim 3] The secondary power supply according to claim 1 or 2 by which 0.5 - 2.5 mol/L and lithium salt are contained in the organic electrolytic solution for the 4th class onium salt 0.5 to 2.0 mol/L.

[Claim 4] The secondary power supply according to claim 1, 2, or 3 in which the lithium content transition-metals oxide containing one or more sorts chosen as a positive electrode from the group which consists of V, Fe, Co, Mn, nickel, W, and Zn, and a lithium is contained.

[Claim 5] The secondary power supply according to claim 4 whose lithium content transition-metals oxide is  $\text{Li}_x\text{Co}_y\text{Ni}_{1-y}\text{O}_2$  or  $\text{Li}_z\text{Mn}_2\text{O}_4$  (however,  $0 < x < 2$ ,  $0 \leq y \leq 1$ ,  $0 < z < 2$ ).

[Claim 6] A lithium content transition-metals oxide is a secondary power supply according to claim 4 or 5 contained five to 80% of the weight all over a positive electrode.

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[Translation done.]

## \* NOTICES \*

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] The withstand voltage of this invention is high, and its capacity is large, and it relates to a secondary power supply with high rapid charge-and-discharge cycle reliability.

[0002]

[Description of the Prior Art] The polarizable electrode to which a positive electrode and a negative electrode make activated carbon a subject is used for the electrode of the conventional electric double layer capacitor. The withstand voltages of an electric double layer capacitor are 2.5-3.3V, when 1.2V and the organic system electrolytic solution will be used, if the drainage system electrolytic solution is used. Since the energy of an electric double layer capacitor is proportional to the square of a withstand voltage, the direction of the organic high electrolytic solution of a withstand voltage is a high energy from the drainage system electrolytic solution.

[0003] However, also with the electric double layer capacitor which used the organic electrolytic solution, the energy density is 1/10 or less [ of rechargeable batteries such as a lead accumulator, ], and improvement in the further energy density is needed. Although it is most effective for improvement in an energy density of an electric double layer capacitor to make voltage high, if voltage is made high, decomposition of the electrolytic solution will take place and a life will be affected greatly.

[0004]

[Problem(s) to be Solved by the Invention] Then, an energy density is high at a high withstand voltage and high capacity, and this invention aims at offering a secondary power supply with high charge-and-discharge cycle reliability.

[0005]

[Means for Solving the Problem] this invention offers the secondary power supply characterized by having the organic electrolytic solution containing the positive electrode containing activated carbon, activated carbon and the negative electrode which contains occlusion and the carbon material from which it may be desorbed for a lithium ion, and the 4th class onium salt and lithium salt.

[0006] In this specification, the thing which joined the positive electrode and charge collector containing activated carbon or activated carbon, and a lithium content transition-metals oxide, and was made to unify is called positive-electrode object. It considers as the definition with the same said of a negative-electrode object. Moreover, although a rechargeable battery and electric double layer capacitor is also one sort of a secondary power supply, on these specifications, the secondary power supply of the specific composition which contains in a negative electrode occlusion and the carbon material from which it may be desorbed for activated carbon and a lithium ion in a positive electrode including activated carbon is only called secondary power supply.

[0007] With the secondary power supply of this invention, at the time of charge, the anion in the electrolytic solution sticks to activated carbon, a lithium ion and the 4th class onium ion stick to activated carbon, and occlusion of the lithium ion is carried out to occlusion and the carbon material from which it may be desorbed in a lithium ion by the negative electrode in a positive electrode. In addition, on these specifications, adsorption means adsorption to the activated carbon of the ion by electric double layer formation at the time of charge, and it calls the reaction accompanied by charge transfer occlusion at the same time ion is incorporated by the electrode. Moreover, it is called desorption that ion separates from activated carbon at the time of electric discharge, and the thing accompanied by charge transfer is called desorption at the same time ion separates.

[0008] At the time of electric discharge of this secondary power supply, the desorption of the anion which is sticking to activated carbon happens, and the desorption of the lithium ion and the 4th class onium ion which are sticking to activated carbon happens by the negative electrode in a positive electrode. The 4th class onium ion remains from activated carbon in part to activated carbon, without a desorption plain-gauze cone carrying out the desorption of all for a lithium ion. Therefore, the potential of the negative electrode at the time of an electric discharge end becomes \*\* from the rest potential of the negative electrode before the first charge.

[0009] Then, if it charges again, adsorption of the 4th class onium ion will take place from \*\*\*\* potential to the above-mentioned activated carbon from the rest potential of activated carbon original. That is, since charge of a negative electrode can be performed in \*\*\*\* potential from a rest potential, the withstand voltage of a secondary power supply is raised.

[0010] If a lithium ion is generally used for occlusion and the carbon material from which it may be desorbed as a negative-electrode active material, although large capacity will be acquired for a lithium ion according to occlusion and the electrochemical reaction from which it is desorbed to a carbon material, a capacity fall is remarkable when it discharges by the high current. However, occlusion and in the case of the charge and discharge by the high current although it \*\*\*\*s, a lithium ion is hardly reacted, respectively at the time of charge according [ occlusion and the carbon material from which it may be desorbed ] the lithium ion of the negative electrode in this invention to a small current comparatively, and electric discharge. In the case of the charge and discharge by the high current, with the secondary power supply of this invention, the physical reaction of the adsorption and desorption of ion to activated carbon occurs. In the case of a physical reaction, although capacity is small, even if it repeats high current charge and discharge, it has few capacity falls.

[0011] That is, in this invention, although it is occlusion, the carbon material from which it may be desorbed, and low capacity about the lithium ion of high capacity, when a capacity fall uses mixture with few activated carbon for a negative electrode to high current charge and discharge, it is high capacity and the capacity fall by high current electric discharge may serve as a few negative electrode.

[0012] The amount of the activated carbon contained in a negative electrode has 10 - 80 desirable % of the weight in activated carbon and a lithium ion in occlusion and a total amount with the carbon material from which it may be desorbed. At less than 10 % of the weight, the fall of the capacity of the secondary power supply by high current electric discharge is remarkable. In \*\*, the capacity of the negative electrode itself becomes small 80% of the weight, and capacity of a secondary power supply cannot be enlarged. Especially the amount of activated carbon has 30 - 70 desirable % of the weight.

[0013] In this invention, the 4th class onium ion and a lithium ion are contained as a cation in the organic electrolytic solution. As the 4th class onium ion, the 4th class ammonium ion or the 4th class phosphonium ion is desirable, and  $4P^+$  ion,  $4(C_2H_5)N^+$  ion,  $3(C_2H_5)(CH_3)N^+$  ion, etc. are especially  $(C_2H_5)$  desirable.

[0014] Moreover, it is the anion of the 4th class onium salt and lithium salt, and the anion contained in the organic electrolytic solution has one or more desirable kinds chosen from the group which consists of  $PF_6^-$ ,  $BF_4^-$ ,  $ClO_4^-$ ,  $N(CF_3SO_2)_2^-$ ,  $CF_3SO_3^-$ ,  $C(SO_2CF_3)_3^-$ ,  $AsF_6^-$ , and  $SbF_6^-$ , and especially its  $BF_4^-$  is desirable. in addition, even if the anion of lithium salt is the same as the anion of the 4th class onium salt, they may differ



[0015] As for the concentration of the 4th class onium salt contained in the organic electrolytic solution, and lithium salt, it is desirable that the 4th class onium salts are [ 0.5 - 2.5 mol/L and lithium salt ] 0.5 - 2.0 mol/L, and it is desirable that lithium salt is especially 0.8 - 1.5 mol/L, and lithium salt is 0.8 - 1.5 mol/L.

[0016] The solvent of the organic electrolytic solution has one or more desirable sorts chosen from the group which consists of ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, a sulfolane, and dimethoxyethane.

[0017] The activated carbon contained in a positive electrode and a negative electrode has the same desirable thing which specific surface area of all is 300-3000m<sup>2</sup>/g, although you may differ but. The raw material of activated carbon and especially activation conditions are not limited, for example, coconuts are mentioned for phenol resin, petroleum coke, etc. as a raw material, and a steam activation method, a melting alkali aktivationsmethode, etc. are mentioned as the activation method.

[0018] In order to raise the capacity of the secondary power supply of this invention, it is desirable that a lithium content transition-metals oxide is contained in a positive electrode. The lithium content transition-metals oxide of the one or more sorts and lithium which are chosen from the group which consists of V, Fe, Co, Mn, nickel, W, and Zn is desirable, and  $\text{Li}_x\text{Co}_y\text{Ni}_{1-y}\text{O}_2$  or  $\text{Li}_z\text{Mn}_2\text{O}_4$  (however,  $0 < x < 2$ ,  $0 \leq y \leq 1$ ,  $0 < z < 2$ .) is especially desirable. The capacity of a positive electrode increases by containing a lithium content transition-metals oxide, and if the lithium ion of a negative electrode increases the amount of occlusion and the carbon material from which it may be desorbed according to it, a secondary power supply will be made more to high capacity.

[0019] 5 - 80% of the weight of the total amount of activated carbon and a lithium content transition-metals oxide of the amount of the lithium content transition-metals oxide in a positive electrode is desirable. The effect that a lithium content transition-metals oxide is contained in a positive electrode as it is less than 5 % of the weight is small, and does not have the voltage of a secondary power supply raised. If it exceeds 80 % of the weight, since the amount of the activated carbon in a positive electrode will decrease relatively, the capacity reduction in a charge-and-discharge cycle becomes remarkable. It is 10 - 60 % of the weight more preferably.

[0020] Moreover, in order to make resistance of a positive electrode low, it is desirable that conductive carbon black or a conductive graphite is contained as electric conduction material all over a positive electrode. As for electric conduction material, at this time, it is desirable to be contained 0.1 to 20% of the weight all over a positive electrode.

[0021] As for the carbon material which can carry out occlusion desorption of the lithium ion contained in a negative electrode in this invention, it is desirable that the spacing of the [002] sides by X diffraction measurement is 0.335-0.410nm. As for the carbon material of 0.410nm \*\*, a spacing tends to deteriorate in a charge-and-discharge cycle. The material which specifically heat-treated petroleum coke, the mesophase pitch system carbon material, or the vapor-growth carbon fiber at 800-3000 degrees C, a natural graphite, an artificial graphite, a difficulty graphite nature carbon material, etc. are mentioned.

[0022] As the production method of a positive-electrode object, after kneading the mixture of activated carbon powder, the carbon black as electric conduction material, and the polytetrafluoroethylene as a binder, for example, it fabricates in the shape of a sheet, and considers as a positive electrode, and there is the method of using an electroconductive glue for a charge collector and fixing this positive electrode to it. Moreover, the varnish which dissolved the polyvinylidene fluoride, the polyamidoimide, the polyimide, etc. as a binder is made to distribute activated carbon powder and carbon black, by the doctor blade method etc., on a charge collector, coating of this may be carried out, and it may be dried and obtained. When a lithium content transition-metals oxide is contained in a positive electrode, the mixture of activated carbon powder and lithium content transition-metals oxide powder is used instead of the above-mentioned activated carbon powder, and it can produce similarly.

[0023] As for the amount of the binder contained in a positive electrode, it is desirable that it is 1 - 20 % of

the weight from the balance of the intensity of a positive-electrode object and properties, such as capacity. Moreover, also as for a negative-electrode object, producing like a positive-electrode object is desirable, and it is [ the amount of the binder contained in a negative-electrode object ] desirable. [ of 1 - 20 % of the weight ] [0024] -

[Example] Next, this invention is not limited by these although an example (Examples 1-4) and the example of comparison (Example 5) explain this invention still more concretely. In addition, the dew-point performed all of production and measurement of the cell in Examples 1-5 in the argon glove box -60 degrees C or less. [0025] [Example 1] After having added ethanol, kneading the mixture which consists the activated carbon of specific-surface-area of 2000m<sup>2</sup>/g obtained by the steam activation method by using phenol resin as a raw material 80% of the weight, and consists a polytetrafluoroethylene of 10 % of the weight considering conductive carbon black as 10 % of the weight and a binder and rolling it out, the vacuum drying was carried out at 200 degrees C for 2 hours, and the electrode sheet with a thickness of 150 micrometers was obtained. This sheet was joined to the aluminum foil using the electroconductive glue which uses a polyamidoimide as a binder, and it heat-treated at 300 degrees C under reduced pressure for 2 hours, and considered as the positive-electrode object. In addition, electrode area was set to 2 24cm.

[0026] Ethanol was added, the mixture which the spacing of the [002] sides acquired by heat-treating petroleum coke 70% of the weight in the activated carbon used for the positive-electrode object is 0.344nm, and become in a lithium ion about occlusion and the carbon material from which it may be desorbed, and it becomes from 10 % of the weight about a polytetrafluoroethylene 10% of the weight considering carbon black as 10 % of the weight and a binder was kneaded, and the electrode sheet with a thickness of 150 micrometers was produced by the same method as a positive electrode. It joined to copper foil like the positive electrode using the electroconductive glue which uses a polyamidoimide as a binder, and this sheet was heat-treated at 300 degrees C under reduced pressure for 2 hours, and was used as the negative-electrode object. In addition, electrode area was set to 2 24cm.

[0027] The above-mentioned positive-electrode object and the above-mentioned negative-electrode object were made to counter through the nonwoven fabric separator made from polypropylene, were pinched, and the element was produced. The solution which dissolved LiBF<sub>4</sub> of 3(C<sub>2</sub>H<sub>5</sub>) (CH<sub>3</sub>) NBF<sub>4</sub> of 1 mol/L and 1 mol/L at propylene carbonate is made into the electrolytic solution, and the aforementioned element was fully infiltrated into this electrolytic solution, and first, by 3.2V, it charged for 24 hours and discharged to after that 1V. Next, initial capacity was measured in the ranges from 3.2V to 1V. Then, by 240mA of charge and discharge currents, the charge-and-discharge cycle examination was performed in the ranges from 3.2V to 1V, the capacity after 2000 cycles was measured, and capacity rate of change was computed. A result is shown in Table 1.

[0028] [Example 2] The negative-electrode object was acquired [ the mixing ratio of the electrode sheet of a negative electrode ] for activated carbon like Example 1 except having changed occlusion and the carbon material from which it may be desorbed, and having changed [ 40 % of the weight and the lithium ion ] the polytetrafluoroethylene for carbon black to 10% of the weight as 10 % of the weight and a binder 40% of the weight. Except having used this negative-electrode object, the element was produced like Example 1 and the electrolytic solution was infiltrated like Example 1. It was similarly estimated as Example 1 using this element. A result is shown in Table 1.

[0029] [Example 3] Activated carbon was carried out 80% of the weight, and the positive-electrode object was acquired [ conductive carbon black ] for 10 % of the weight and the polytetrafluoroethylene like Example 1 instead of 10% of the weight of mixture except having used conductive carbon black for LiCoO<sub>2</sub> 20% of the weight 60% of the weight, and having used [ activated carbon ] 10% of the weight of mixture for 10 % of the weight and the polytetrafluoroethylene.

[0030] Except having used the above-mentioned positive-electrode object, the element was produced like Example 1 and it was similarly estimated as Example 1. A result is shown in Table 1.

[0031] [Example 4] The positive-electrode object was acquired like Example 3 except having used  $\text{LiCo}_0.2\text{nickel } 0.8\text{O}_2$  instead of  $\text{LiCoO}_2$ . Except having used this positive-electrode object, the element was produced like Example 1 and it was similarly estimated as Example 1. A result is shown in Table 1.

[0032] [Example 5] Except having used also for the positive-electrode object the positive-electrode object acquired by the negative-electrode object in Example 1, the element was produced like Example 1, capacity was measured like Example 1, and it was similarly estimated as Example 1. A result is shown in Table 1.

[0033]

[Table 1]

	初期容量 (mAh)	容量変化率 (%)
例1	4.83	-8.6
例2	6.32	-9.8
例3	11.7	-9.9
例4	12.6	-10.2
例5	3.64	-54.7

[0034]

[Effect of the Invention] the secondary power supply of this invention -- a negative electrode -- setting -- the charge and discharge in comparatively big current -- the 4th class onium ion -- adsorption and desorption -- carrying out -- the charge and discharge in comparatively small current -- a lithium ion -- occlusion and the carbon material from which it may be desorbed -- a lithium ion -- occlusion -- it \*\*\*\*s Therefore, in the lithium ion by the charge and discharge in big current, there is little degradation of occlusion and the carbon material from which it may be desorbed, and it is excellent in the rapid charge-and-discharge property.

[0035] Moreover, since the potential of the activated carbon contained in a negative electrode is \*\* from the rest potential, the secondary power supply of this invention has a high withstand voltage. Furthermore, since occlusion and the carbon material from which it may be desorbed are contained in the negative electrode in the lithium ion, it is high capacity.

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[Translation done.]